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(54) Title: FAST DRYING JET INK COMPOSITION

(57) Abstract

The present invention provides a fast drying jet ink composition comprising an organic solvent, a colorant, a polyamine which is substantially free of alkoxysilyl groups, and an acidic resin having an acid number of from about 10 to about 120. The jet ink composition can be used to print on glass surfaces that have a condensation of moisture on them. The printed messages do not easily rub off after exposure to humid conditions. The messages printed on glass can be easily washed off by a caustic solution.

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FAST DRYING JET INK COMPOSITION

The present invention relates to a fast drying jet printing ink composition suitable for printing on glass surfaces which may be exposed to humid conditions during printing. The messages printed on glass surfaces are resistant to exposure to humid conditions.

Ink jet printing is a well-known technique by which printing is accomplished without contact between the printing device and the substrate on which the printed characters are deposited. Briefly described, ink jet printing involves the technique of projecting a stream of ink droplets to a surface and controlling the direction of the stream electronically so that the droplets are caused to form the desired printed message on that surface.

The technique of ink jet printing or non-contact printing is particularly well suited for application of characters onto irregularly shaped surfaces, including, for example, glass, metal, or plastic containers, generally used for holding beverage, cosmetic, pharmaceutical, liquor, and health care products.

Reviews of various aspects of ink jet printing can be found in the following publications: Kuhn et al., *Scientific American*, April, 1979, 162-178; and Keeling, *Phys. Technol., 12(5)*, 196-303 (1981). Various ink jet apparatuses are described in the following U.S. patents: 3,060,429, 3,298,030, 3,373,437, 3,416,153, and 3,673,601.

In general, an ink jet ink composition must meet certain rigid requirements to be useful in ink jet printing operations. These relate to viscosity, resistivity, solubility, compatibility of components and wettability of the substrate. Further, the ink must be quick-drying and smear resistant, resist rubbing, and be capable of passing through the ink jet nozzle without clogging, and permit rapid cleanup of the machine components with minimum effort.

In addition, the ink must meet certain other requirements. Many beverage manufacturers

fill the containers with chilled beverages, frequently under humid conditions that promote condensation of moisture on the containers. The moisture that condenses on the container surfaces poses a severe problem in obtaining ink penetration, good adhesion, and abrasion resistance of the printed messages. Thus, the jet ink should allow printing on these containers in the presence of the condensation, and the printed messages also should not be damaged by the condensation. In addition, if the containers are immersed in ice water for chilling, the messages should not disintegrate or be damaged by the ice water. Moreover, the bottles may be exposed to warm and humid conditions during warehousing and shipping to different parts of the country and in different seasons. The messages should not be damaged by the hot and cold humid conditions. Further, the messages should be removable by a caustic wash in order to allow reuse of the returned glass bottles.

Many of the known ink jet ink compositions are not suitable for printing on glass under humid conditions, or do not provide water resistant printed messages on glass surfaces. Only a few ink compositions are reported to be suitable for printing on glass surfaces under humid conditions. For example, U.S. Patent 5,693,127 discloses a jet ink comprising a binder, a colorant, a liquid vehicle and an adhesion promoter which is an alkoxysilyl polyalkylene-imine. Although the patent states that the ink is suitable for printing on glass bottles having a condensation thereon, certain difficulties are encountered in following its teachings. For example, the alkoxysilyl polyalkylene-imine adhesion promoter does not appear to be commercially available, and the patent does not teach those of ordinary skill in the art how to make this adhesion promoter. Further, the stability of the ink composition containing alkoxysilylated polyalkylene-imines under certain conditions remains uncertain.

U.S. Patent 5,596,027 discloses an ink jet ink composition comprising an ink carrier, a colorant, a polyamine, and an acidic resin. This ink composition is capable of producing condensation and moisture resistance images on glass bottles. Although the claims are directed to

solvent-based as well as water-based ink compositions, the patent does not suggest the specific advantage, the short drying time, that has been obtained herein by the use of organic solvents as the ink carrier. Water-based inks take a relatively long time to dry on glass substrates. Drying times greater than 10 seconds may be necessary with water-based inks.

Thus, there exists a need for a jet ink composition meeting certain critical performance requirements. There exists a need for jet ink composition that provide high quality messages on container surfaces, especially glass surfaces. There exists a need for a jet ink composition which can be printed on glass surfaces which may have moisture condensation on them. There exists a need for a jet ink composition whose printed messages do not smear, rub off, or otherwise degrade after exposure to ice water. Further, there exists a need for a jet ink composition whose printed messages do not smear, rub off, or otherwise degrade after exposure to hot and cold humid conditions. There further exists a need for a jet ink composition whose printed messages on glass surfaces can be washed off by a caustic solution.

It is therefore an object of the present invention to provide a jet ink composition that provides high quality messages on various surfaces, particularly glass surfaces which may have a condensation of moisture on them. It is a further object of the present invention to provide a jet ink composition whose printed messages do not smear, rub off, or otherwise degrade when exposed to hot and cold humid conditions. It is also an object of the present invention to provide a jet ink composition whose printed messages do not smear, rub off, or otherwise degrade when exposed to ice water. It is a further object of the present invention to provide a jet ink composition whose messages on glass surfaces can be washed off readily using a caustic solution.

The present invention provides a jet ink composition comprising an organic solvent, a colorant, a polyamine which is free or substantially free of alkoxysilyl groups, and an acidic resin having an acid number of from about 10 to about 120. The acid number is expressed in mg KOH/g of resin. The present invention further provides a jet ink composition comprising an organic

solvent, a colorant, an acidic resin, and a polyamine selected from the group consisting of a polyalkyleneamine, an aminoacrylic polymer, and a dendrimer.

The jet ink composition of the present invention has an advantage that it can produce high quality messages on various surfaces. The jet ink composition makes possible printing on glass surfaces which have a condensation of moisture thereon. The printed messages on glass do not smear or rub off after exposure to humid conditions. Further the printed messages do not smear or rub off after exposure to ice water, cold and hot humid conditions. The messages printed on glass can be washed off by a caustic solution.

The colorant used in the ink composition of the present invention includes a dye or a pigment. The ink composition of the present invention may additionally include surfactants, humectants, plasticizers, defoamers, and electrolytes.

The present invention further provides an improved process of jet printing on glass surfaces messages having condensation and water resistance, the improvement comprising using the ink composition of the present invention in the jet printing process.

The ink composition of the present invention, in general, exhibits the following characteristics for use in ink jet printing systems: (1) a viscosity of from about 1.5 centipoises (cps) to about 7 cps at 25°C; (2) an electrical resistivity of from about 50 ohm-cm to about 2000 ohm-cm; and (3) a sonic velocity of from about 1100 meters/second to about 1700 meters/second.

The jet ink composition of the present invention has the advantage that it dries rapidly from substrate surfaces, particularly glass surfaces, which allows high speed printing. The drying time of the jet printed message is less than 10 seconds, preferably less than about 2 seconds, and more preferably about 1 second or less.

Preferably the colorant used in the ink composition includes a dye or a pigment. The ink composition of the present invention may additionally include surfactants, humectants, plasticizers, electrolytes, and defoamers.

The ink composition of the present invention can be prepared by any suitable method. For instance, the components of the composition can be combined and mixed in a suitable mixer or blender. A detailed discussion of each of the components and the characteristics of the inventive ink composition are set forth below.

ORGANIC SOLVENT

Any suitable organic solvent can be used as the ink carrier of the ink composition of the present invention, and preferably a low boiling organic solvent or a mixture of such organic solvents is used as the ink carrier. Examples of suitable organic solvents include ketones, alcohols, esters, ethers, and amides, and preferably lower ketones, lower alcohols, and mixtures thereof. Thus, methyl ethyl ketone, ethanol, and mixtures of them are examples of preferred ink carriers.

Any suitable amount of ink carrier can be used. Typically the carrier is used in an amount of up to about 95%, preferably in an amount of from about 35% weight to about 85% by weight, and more preferably in an amount of from about 80% by weight to about 85% weight of the ink composition.

POLYAMINE

The ink composition of the present invention comprises a polyamine that is free or substantially free of alkoxysilyl groups. It is believed that the amino group of the polyamine interacts with the acidic resin to provide a durable printed message that resists condensation of moisture and resists smearing or damage when exposed to ice water. The interaction between the polyamine and the acidic resin has not been fully understood, and it is believed that it may involve interactions such as formation of covalent, ionic, hydrogen bonding, and/or other interactions such as van der Waals interactions, dipole-dipole interactions, dipole-induced dipole interactions, or combinations thereof. An example of an ionic interaction is the formation of an ammonium

carboxylate salt.

It is also believed that polyamine and the surface of the substrate interact suitably to provide improved adhesion between the substrate surface and the components of the printed message. Thus, it is believed that the surface groups, such as the amino groups on the polyamine, interact with the surface groups on the substrate.

The polyamine has at least two amino groups per molecule. It may be a small molecule such as ethylenediamine, or a polymeric molecule such as polyethyleneimine. The molecule may be linear, branched, cross-linked, or three-dimensional.

A preferred class of polyamine is a polyalkyleneamine. Another preferred class of polyamine is an aminoacrylic polymer, for example, a copolymer of methylmethacrylate and dimethylaminoethyl methacrylate described in U.S. Patent 4,834,799. Yet another example of a preferred class of polyamines is a dendrimer.

Examples of suitable polyamines include N,N'-bis(3-aminopropyl)-1,2-ethylenediamine, 1,4-bis(3-aminopropyl)piperazine, N,N'-bis(3-aminopropyl)-1,4-butanediamine, nitrilotrisethylamine, N,N'-(diaminoethyl)piperazine, piperazinylethylethylenediamine, aminoethyl-triethylenetetramine, aminoethylpiperazinylethyl-ethylenediamine, piperazinylethyldiethylenetriamine, and polyalkyleneamines such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and pentaethylenehexamine, and mixtures thereof.

Dendrimers are radially symmetrical molecules of a STARBURST™ topology comprised of an initiator core, such as nitrogen, ethyleneimine, and the like, interior layers attached to the core and comprised of a suitable number of arms, for instance, two to four arms, each arm being comprised of repeating units with the number of repeating units in each arm being considered the generation of the dendrimer, and terminal groups functionality, such as, for example, a primary amine attached to the outmost generation, which dendrimers are illustrated, for example, in U.S.

patents 4,507,466; 4,631,337, 4,558,120, 4,568,737, and 4,587,329, and in Tomalia et al., *Angewandte Chemie, Int. Ed. Engl. 29*, 138 (1990). The size and shape of the STARBURST dendrimer molecule and the functional groups present in the dendrimer molecule can be controlled by the choice of the initiator core, the number of generations, and the choice of repeating units employed at each generation.

The choice of the dendrimer components can affect the properties of the dendrimers. The initiator core type can affect the dendrimer shape producing, for example, spheroid-shaped dendrimers, cylindrical- or rod-shaped dendrimers, or ellipsoid-shaped dendrimers. Sequential building of generations determines the dimensions of the dendrimers and the nature of its interior. Examples of suitable core materials include ammonia, polyfunctional alcohols, such as pentaerythritol or tris-(hydroxymethyl)ethane, 1,1,1-tris-(4'-hydroxypheyl)-ethane, polyfunctional amines, such as ethylene diamine, linear polyethyleneimines, and the like. The chemical functionality of the repeating unit in the interior layers can include, for example, amidoamines, such as aminoethyl acetamide, imines, such as diethylene diimine, or ethers like those obtained from materials such as, for example, 3,5-dihydroxyethyl benzyl alcohol. The terminal functionalities include, for example, amino groups, hydroxyl groups, carboxylic acid groups, carboxylates, esters, amides, phosphates, sulfonates, and the like.

The synthesis of dendrimers usually occurs by a divergent approach that involves the initial reaction of a monomer with the initiator core, followed by exhaustive reaction of the resulting functional groups with a difunctional compound, such as a diamine, including, for example, ethylene diamine, to afford the next generation of reactive amino groups. Thus, for example, ethylene diamine can be suitably reacted first with methyl acrylate to produce a compound such as N,N,N',N'-tetra(methoxycarbonylethyl)-ethylenediamine. The aforesaid compound can be reacted in the next step with ethylene diamine to produce an amidoamine dendrimer having a generation number of zero, a molecular weight of 517, and four primary amino groups at the surface.

Repetition of the above two-step procedure leads to subsequent generations.

An alternate synthetic route uses a convergent growth synthesis as described in detail in Hawker et al., *J. Amer. Chem. Soc., 112*, 7638 (1990).

The dendrimer may have other groups or segments, in addition to amino groups. For instance, the dendrimer may have a dye covalently attached to it, or it may have certain functional groups grafted onto it.

Preferred dendrimers for use in the preparation of the ink composition of the present invention include those having terminal amine functionality at the surface. It is further preferred that the dendrimer has a molecular weight in the range from about 300 to about 100,000, a generation number of from 0 to 10, a surface amine group concentration of from about 3 to about 4,100, and a molecular diameter of from about 10 A to about 10,000 A. It is also more preferred that the dendrimer has a molecular weight in the range from about 500 to about 5,000, a generation number of from 0 to about 2, and a surface group concentration of from about 4 to about 16. It is also preferred that the polydispersity index (Mw/Mn) of the dendrimer is low, preferably in the range of from about 1.1000 to about 1.0001, and more preferably in the range of from about 1.001 to about 1.0001. For additional details on the dendrimers, see U.S. Patent 5,596,027, column 6, lines 39-62, the disclosure of which is incorporated herein by reference.

Any suitable amount of the polyamine can be used. The polyamine is used preferably in an amount of from about 0.01% to about 5% by weight, and more preferably in an amount of from about 0.1% to about 0.5% by weight of the ink composition.

COLORANT

The ink composition of the present invention comprises a colorant. Any suitable colorant, dye or pigment, can be used. An example of a suitable dye is C.I. Solvent Black 29, which is available as ORASOL BLACK RLI™ from Ciba-Geigy. For examples of pigments and additional

examples of dyes, see U.S. Patent 5,596,027, column 7, line 12, to column 9, line 3, the disclosure of which is incorporated herein by reference.

The colorant can be used in the ink composition in an amount required to produce the desired color intensity, contrast and readability. The colorant is used preferably in an amount of from about 1% to about 10% by weight, and more preferably in an amount of from about 3% to about 6% by weight of the ink composition.

ACIDIC RESIN

The ink composition of the present invention comprises an acidic resin. Any suitable polymeric resin having a carboxyl, sulfonic, or phosphonic acid group can be used, with carboxyl group being preferred. Preferred acidic resins are those having an acid number in the range of from about 10 to about 120, and the more preferred acidic resins have an acid number in the range of from about 50 to about 80.

The acidic resins than can be used in the ink composition include organic solvent soluble or organic solvent dispersible resins. Thus, the resin may form a true solution or a colloidal suspension that may be used if filterable without substantial separation through a filter having a pore size substantially smaller than the printer capillary tube, for example through a filter having a pore size of about one micron.

Examples of acidic resins that can be used in the ink composition of the present invention include acrylic resins bearing carboxyl groups. Examples of suitable such acrylic resins include the SURCOL™ 836 resin available from Allied Colloids Co. in Suffolk, Virginia. The SURCOL 836 resin has an acid number of 63, a number average molecular weight of about 26,000 and a weight average molecular weight of about 46,000. Other examples of such acrylic resins include JONCRYL™ 611 and JONCRYL 586, available from S.C. Johnson Co., in Racine, Wisconsin. JONCRYL 611 has an acid number of 53 and JONCRYL 586 has an acid number of 108. Yet

another example of a suitable acidic acrylic resin is CARBOSET™ 527 available from B.F. Goodrich Specialty Chemicals Co. in Cleveland, Ohio. CARBOSET 527 has an acid number of 80 and a weight average molecular weight of about 40,000. A further example of a suitable acidic acrylic resin is NEOCRYL™ B-817 available from Zeneca Resins, Inc., in Wilmington, Delaware. NEOCRYL B-817 is a copolymer comprising methylmethacrylate and ethylacrylate, and has an acid number of 55 and a weight average molecular weight of about 20,000.

The acidic resin can be used in any suitable amount. The acidic resin is preferably used in an amount of from about 3% to about 30% by weight, and more preferably in an amount of from about 7% to about 15% by weight of the ink composition.

SURFACTANT

The jet ink composition of the present invention can further include a surfactant to optimize the wetting and drying characteristics of the ink. Any suitable surfactant can be employed, for example, fluoroaliphatic polymeric esters and polyalkylene oxide modified polydimethylsiloxanes. Examples of suitable surfactants include SILWET™ 7622, which is a polyethylene oxide modified polydimethylsiloxane, available from OSI Specialties, Inc. in Danbury, Connecticut, and FC 430, which is a fluoroaliphatic polymeric ester, available from 3M Co.

The surfactant can be used in any suitable amount, preferably in an amount of up to about 2% by weight, and more preferably in an amount of from about 0.01% to about 1% by weight of the ink composition.

PLASTICIZER

The jet ink composition of the present invention can also include a plasticizer to improve the durability of the printed message. Any suitable plasticizer can be used. For example, Plasticizer 8, which is an *o,p*-mixture of N-ethyltoluenesulfonamide available from Monsanto Co.,

can be used.

The plasticizer can be used in any suitable amount, preferably in an amount of up to about 2% by weight, and more preferably in an amount of from about 0.01% to about 1% by weight of the ink composition.

HUMECTANT

The ink composition of the present invention may preferably include a humectant to prevent drying of the ink on the print head during the printing operation, as well as during storage of the ink. Humectants are hydrophilic solvents having high boiling points, preferably above 100°C, and more preferably in the range of from about 150°C to about 250°C. Any suitable humectant known to those of ordinary skill in the art can be used. Examples of suitable humectants include glycols such as ethylene glycol, propylene glycol, glycerin, diglycerin, diethylene glycol, and the like, glycol ethers such as ethylene glycol dimethyl ether, ethylene glycol diethylether, propyleneglycol methylether cellosolve, diethylene glycol monoethylether (Carbitol), diethylene glycol dimethylether, and diethylene glycol diethylether, dialkyl sulfoxides such as dimethyl sulfoxide, and other solvents such as sulfolane, N-methyl pyrrolidinone, and the like.

The humectant can be used in an amount of up to about 5% by weight, and more preferably in an amount of up to about 2% by weight of the ink composition.

DEFOAMER

The ink composition of the present invention can further include a defoamer to prevent foaming of the ink during its preparation, as well as during the printing operation. Any suitable defoamer known to those of ordinary skill in the art, for example, polysiloxane defoamers, can be used. An example of a polysiloxane defoamer is BYK™ 065 from BYK-Chemie, in Wallingford, Connecticut.

The defoamer can be present in the jet ink composition of the present invention in an amount effective to prevent foaming of the jet ink during preparation and use. The defoamer can be used in an amount of from about 0.1% by weight to about 1% by weight, preferably in the range of from about 0.25% by weight to about 0.35% by weight.

The jet ink composition of the present invention may also include a suitable silane to further improve the adhesion of the message to glass substrates. An example of a suitable silane is an epoxysilane such as the Silane A-187, available from OSI Specialties, Inc., which is γ-glycidoxypropyl trimethoxysilane. The jet ink composition may further include if necessary an electrolyte to adjust its electrical conductivity. Any suitable electrolytes known to those of ordinary skill in the art can be used.

The jet ink composition of the present invention can be printed on a variety of glass bottles. Examples of glass bottles include beer bottles, the returnable and the non-returnable varieties. The jet ink of the present invention may be jet applied onto a variety of glasses, including soda-lime glasses, borosilicate glasses, alumino-silicate glasses, lead glasses, borate glasses, and the like. The above specified types of glass containers may contain an additional coating.

The following illustrative examples further illustrate the present invention but, of course, should not be construed as in any way limiting its scope.

EXAMPLE 1

This example illustrates the preparation of an embodiment of the present invention wherein pentaethylenehexamine was employed as the polyamine and SURCOL 836 was employed as the acidic resin. The following ingredients were employed in the amounts indicated. Herein below IPA stands for isopropanol.

Ingredients	Parts
Methyl ethyl ketone (MEK, Exxon)	629
Ethanol CDA-19 200 Proof (EMCO Chemical)	200
Pentaethylenehexamine, 10% in IPA (Aldrich)	20
SURCOL 836 (Allied Colloids)	100
ORASOL BLACK RLI (Ciba-Geigy)	50
FC-430, 10% in MEK (3M)	1
Total	1000

The ink was printed on COCA-COLA™ and FANTA™ glass bottles in a 95°F/90% relative humidity chamber. Prior to printing, the bottles were cleaned by washing them with a 3% sodium hydroxide solution at 60°C for 5 minutes followed by rinsing with deionized water. The bottles were then filled with ice water. An air knife was used to remove any excess water drops on the surface of the bottles. Messages were jet printed below the fill line one minute after filling the bottles. Due to the high humidity of the environment and the low temperature of the bottles, a significant amount of moisture condensation occurred on the bottles before as well as after the printing.

The following tests were carried out on the printed bottles:

Chamber Rub Test: The printed message was rubbed with the thumb using heavy pressure one minute after printing and the number of rubs needed to remove the message was noted. The messages needed at least 10 rubs to be removed from the glass surface.

Ice Water Test: The bottles were immersed in ice water for a period of at least 16 hours after the messages on the bottles were allowed to dry for at least few hours at ambient conditions. The messages were rubbed with the thumb using heavy pressure. The messages needed 7 rubs to be removed from the glass surface.

Caustic Wash Test: The bottles were allowed to dry in the ambient for at least one hour and then immersed in a bath containing 3% sodium hydroxide at 60°C for 5 minutes. In a majority of cases, the messages were lifted off by the caustic solution. In some cases where the messages were not completely removed by the caustic solution, the bottles were taken out of the caustic bath after the 5 minute immersion and placed in a deionized water bath. These messages were completely removed from the glass surface by the water bath.

EXAMPLE 2

This example illustrates the preparation of another embodiment of the present invention

wherein pentaethylenehexamine was employed as the polyamine and SURCOL 836 was employed as the acidic resin. The following ingredients were employed in the amounts indicated.

Ingredients	Parts
Methyl ethyl ketone (Exxon)	748
Ethanol CDA-19 200 Proof (EMCO Chemical)	90
Pentaethylenehexamine, 10% in IPA (Aldrich)	20
SURCOL 836 (Allied Colloids)	80
ORASOL BLACK RLI (Ciba-Geigy)	40
Plasticizer 8 (Monsanto)	10
FC-430, 10% in MEK (3M)	10
BYK 065 (BYK-Chemie)	2
Total	1000

The glass bottles were jet printed and the printed messages were tested as set forth in Example 1. The messages had good rub resistance and passed the caustic wash test. In the chamber rub test as well as the ice water test, the messages needed more than 10 rubs to be removed.

EXAMPLE 3

This example illustrates the preparation of another embodiment of the present invention wherein STARBURST generation 2 was employed as the polyamine and SURCOL 836 was employed as the acidic resin. The following ingredients were employed in the amounts indicated.

Ingredients	Parts
Methyl ethyl ketone (Exxon)	763
Ethanol CDA-19 200 Proof (EMCO Chemical)	90
STARBURST Generation 2, 49.51% in methanol (Dendritech)	5
SURCOL 836 (Allied Colloids)	80
ORASOL BLACK RLI (Ciba-Geigy)	40
Plasticizer 8 (Monsanto)	10
FC-430, 10% in MEK (3M)	10
BYK 065 (BYK-Chemie)	2
Total	1000

The glass bottles were jet printed and the printed messages were tested as set forth in Example 1. The messages had good rub resistance and passed the caustic wash test. In the chamber rub test as well as the ice water test, the messages needed more than 10 rubs to be removed.

EXAMPLE 4

This example illustrates the preparation of another embodiment of the present invention

wherein a methyl methacrylate/dimethylaminoethyl methacrylate copolymer was employed as the polyamine and SURCOL 836 was employed as the acidic resin. The following ingredients were employed in the amounts indicated.

Ingredients	Parts
Methyl ethyl ketone (Exxon)	742
Ethanol CDA-19 200 Proof (EMCO Chemical)	100
Methyl methacrylate/dimethylaminoethyl methacrylate (70/30) copolymer, 35.5% in MEK	16
SURCOL 836 (Allied Colloids)	80
ORASOL BLACK RLI (Ciba-Geigy)	40
Plasticizer 8 (Monsanto)	10
FC-430, 10% in MEK (3M)	10
BYK 065 (BYK-Chemie)	2
Total	1000

The glass bottles were jet printed and the printed messages were tested as set forth in Example 1. The messages had good rub resistance and passed the caustic wash test. In the chamber rub test as well as the ice water test, the messages needed more than 10 rubs to be removed.

The present invention provides a jet ink composition wherein methyl ethyl ketone is present in an amount of from about 30% by weight to about 80% by weight of the ink composition, ethanol is present in an amount of up to about 50% by weight of the ink composition, a polyamine that is free or substantially free of alkoxysilyl groups is present in an amount of from about 0.1% by weight to about 0.5% by weight of the ink composition, an acidic resin is present in an amount of from about 5% by weight to about 20% by weight of the ink composition, a dye is present in an amount of from about 3% by weight to about 6% by weight of the ink composition, a surfactant is present in an amount of from about 0.01% by weight to about 1% by weight of the ink composition, and a humectant is present in an amount of up to about 2% by weight of the ink composition.

The present invention further provides an improved process for jet printing on glass surfaces messages having resistance to water comprising directing a stream of ink droplets to the surface and controlling the direction of the droplets so as to form the messages, the improvement comprising directing a jet ink composition comprising an organic solvent, a colorant, a polyamine which is free or substantially free of alkoxysilyl groups, and an acidic resin having an acid number of from about 10 to about 120.

CLAIMS:

1. A jet ink composition comprising an organic solvent, a colorant, a polyamine which is free or substantially free of alkoxysilyl groups, and an acidic resin having an acid number of from 10 to 120.

2. A jet ink composition as claimed in claim 1, wherein said composition has a viscosity of from 1.5 centipoises (cps) to 7 cps at 25°C, an electrical resistivity of from 50 ohm-cm to 2000 ohm-cm, and a sonic velocity of from 1100 meters/second to 1700 meters/second.

3. A jet ink composition as claimed in claim 1 or 2, wherein said colorant is a dye.

4. A jet ink composition as claimed in claim 3, wherein said dye is Solvent Black 29.

5. A jet ink composition as claimed in any one of the preceding claims, wherein said organic solvent is selected from the group consisting of ketones and alcohols.

6. A jet ink composition as claimed in claim 5, wherein said organic solvent is selected from the group consisting of methyl ethyl ketone, ethanol, and combinations thereof.

7. A jet ink composition as claimed in any one of the preceding claims, wherein said acidic resin has an acid number of from 50 to 80.

8. A jet ink composition as claimed in any one of the preceding claims, wherein said polyamine is selected from the group consisting of pentaethylenehexamine, dendrimers of generations 0, 1 and 2, and copolymers of methylmethacrylate and dimethylaminoethylmethacrylate.

9. A jet ink composition as claimed in any one of the preceding claims, wherein said acidic resin is a carboxylated acrylic polymer.

10. A jet ink composition as claimed in any one of the preceding claims, which further includes a surfactant.

11. A jet ink composition as claimed in any one of the preceding claims, which further includes a humectant.

12. A jet ink composition as claimed in claims 6, 10 and 11, wherein said methyl ethyl ketone is present in an amount of from 30% by weight to 80% by weight of the ink composition, said ethanol is present in an amount of up to 50% by weight of the ink composition, said polyamine is present in an amount of from 0.1% by weight to 0.5% by weight of the ink composition, said acidic resin is present in an amount of from 5% by weight to 20% by weight of the ink composition, said dye is present in an amount of from 3% by weight to 6% by weight of the ink composition, said surfactant is present in an amount of from 0.01% by weight to 1% by weight of the ink composition, and a humectant is present in an amount of up to 2% by weight of the ink composition.

13. A jet ink composition comprising an organic solvent, a colorant, an acidic resin, and a polyamine selected from the group consisting of a polyalkyleneamine, an aminoacrylic polymer, and a dendrimer.

14. In an improved process for jet printing on glass surfaces messages having resistance to water comprising directing a stream of ink droplets to said surface and controlling the direction of said droplets so as to form the messages, the improvement comprising directing a jet ink composition as claimed in any one of the preceding claims.

INTERNATIONAL SEARCH REPORT

Intern. al Application No
PCT/GB 99/00373

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 731 149 A (IMAJE SA) 11 September 1996 see page 4, line 35 - line 37; table 1 see page 4, line 53 - page 6, line 6	1
A	US 5 254 159 A (GUNDLACH KURT B ET AL) 19 October 1993 see column 4, line 62 - column 5, line 43 see column 12, line 55 - column 14, line 36	1,13
A	US 5 596 027 A (MEAD SHARON B ET AL) 21 January 1997 cited in the application	1,13

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 May 1999	18/05/1999

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. al Application No
PCT/GB 99/00373

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0731149 A	11-09-1996	FR 2731433 A	13-09-1996
		AU 701939 B	11-02-1999
		AU 4581296 A	19-09-1996
		CA 2170849 A	09-09-1996
		CN 1139689 A	08-01-1997
		JP 8253722 A	01-10-1996
		US 5744519 A	28-04-1998
US 5254159 A	19-10-1993	BR 9305056 A	05-07-1994
		EP 0604097 A	29-06-1994
		JP 2583735 B	19-02-1997
		JP 6228483 A	16-08-1994
		MX 9307326 A	30-06-1994
		US 5360472 A	01-11-1994
US 5596027 A	21-01-1997	AU 6310296 A	10-02-1997
		WO 9703137 A	30-01-1997